Studies on Rheological Properties of Foodstuffs

Part. II. The Viscosities of Concentrated Aqueous Solutions of Methylcellulose

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The investigation of this series has aimed to describe some rheological properties of foodstuffs and to relate them to their structures and compositions. The earlier paper[1] has reported the calibration of viscometers. In the present work, we carry out viscometric studies on the aqueous solutions of methylcellulose.

Methylcellulose is a kind of cellulose-ethers and used extensively in food products as thickener, stabilizer, swelling agent, coating agent, molding agent, and binder.

The results show that the mode of the flow of the solution is thixotropic below the temperature of ca. 50°C and dilatant over the temperature. Moreover, the viscosities of benzylalcohol solution of the same sample were measured and compared with the results of the aqueous solutions.

EXPERIMENTAL

Viscometer. The concentric cylinder viscometer used was the Shimadzu Universal Rheometer Model UR-1, which was a Couette type viscometer. The viscometer was calibrated by using the aqueous solutions of sucrose.[1]

Materials. Methylcellulose was a product of Shinetsu Chemical Ind. (trade name "Metolose 90 SH 15000"), of which density was 1.31 g/cm^3 and the gelling temperature ca. 90°C. The white powders of the sample was used without further purification. Benzylalcohol was certified reagent grade from Kokusan Kagaku Co., Ltd. and used without further purification.

RESULTS and DISCUSSION

Fig. 1 shows an example of the diagrams, which indicates the relationship between the angular velocities of cup and the distortion angles of wire, θ, obtained by the viscometer. From the diagrams obtained we can calculate the torque, M, on cylinders due

$$M = K\theta. \qquad (1)$$

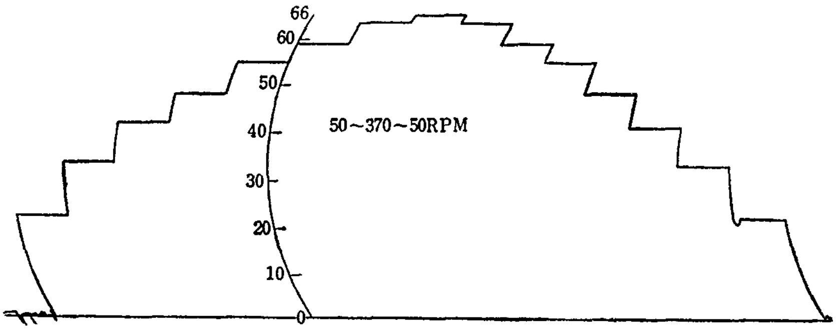

Fig. 1 The diagram obtained by the concentric cylinder viscometer, $2R_1=3.9$cm, $2R_2=4.0$cm and $L=5.0$cm. The diameter of the wire is 0.6mm. The concetration of the aqueous solution is 1.0%, and the temperature is 25°C.

to viscous resistance according to the equation.(1), where K is the wire constant. The apparent viscosity, η_a is given by the following equaion(2).

$$\eta_a = M(R^2_2 - R_1^2)/4\pi R^2_1 R^2_2 L\Omega$$
$$= F(1-1/s^2)/2\Omega \cdots\cdots (2)$$

where R_1 is radius of inner cylindr (bob) and R_2, that of outer cylinder (cup), respectively. L is the length of inner cylinder ; Ω, the angular velocity of cup relative to bob; $s=R_2/R_1$, radius ratio, and $F=M/2\pi R^2_1 L$, shearing stress at bob.

The plots of 2Ω versus $F(1-1/s^2)$ of the aqueous solutions below 50°C are shown in Fig. 2. From the fact that the plots have the curvatures toward uppers, it seems likely that the mode of the flow in the range of the temperature is thixotropic. The destruction of the structure in the solution increases with an increase in the concentration and with a decrease in the temperature as shown in Fig. 2. Also it is conceivable that the thixotropic recovery time of the solutions are very short, because the

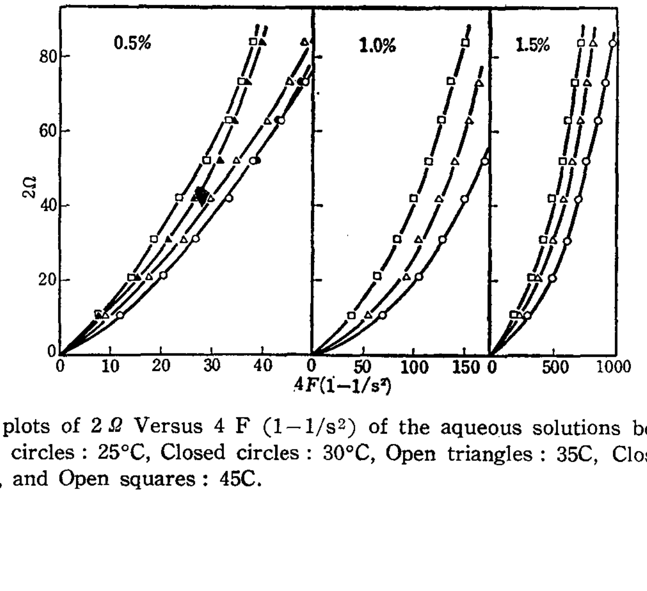

Fig. 2 The plots of 2Ω Versus $4F(1-1/s^2)$ of the aqueous solutions below 50°C. Open circles : 25°C, Closed circles : 30°C, Open triangles : 35C, Closed triangles : 40°C, and Open squares : 45C.

hysteresis loop has not been observed in all measurements.

Fig. 3 shows an example of the plots of the apparent fluidity, φ_a, which is simply the reciprocal of the apparent viscosity, versus 4 F of the aqueous solutions. The figure also shows the character of thixotropy ; the apparent fluidity increases with the

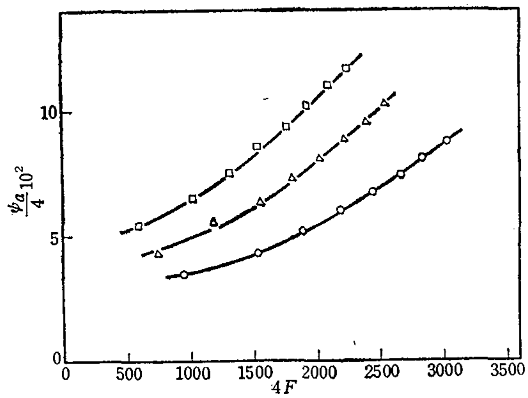

Fig. 3 Variaton of the apparent fluidity, φ_a, with shearing stress, F, for the 1.5% aqueous solution.
Open circles : 25°C, Open triangles : 35°C, and Open squares : 45°C.

increasing shearing stress. The character seems to indicate a presence of submicrosopic molecular aggregates of methyecllulose and a presence of strong hydrogen bondings between water molecules and the molecular aggregates.

For Non-Newtonian liquid, the rate of shear, g(F), can be expressed as follows;[2]

$$g(F) = 2\Omega[1 + \Delta(F)]/(1 - 1/s^2), \cdots\cdots\cdots\cdots (3)$$

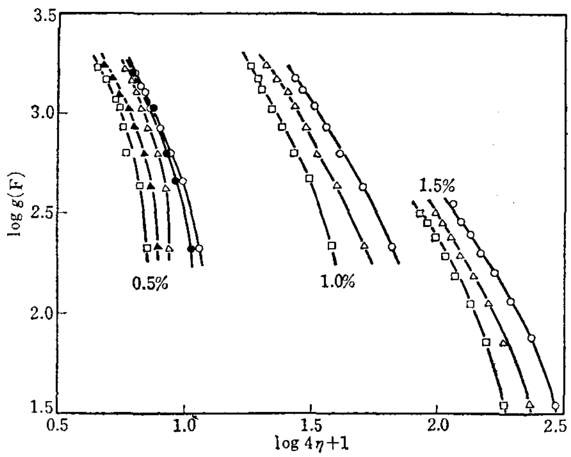

Fig.4 The plots of log g(F) versus log 4 η for the aqueous solutions below 50°C.
Open circles: 25°C, Closed circles: 30°C, Open triangles: 35°C, Closed triangles: 40°C, and Open squares: 45°C.

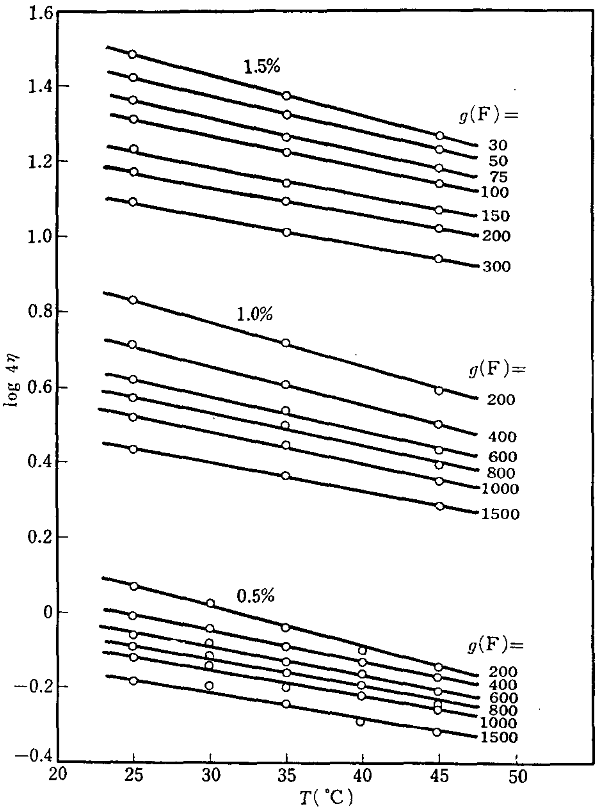

Fig. 5 The plots of log 4 η versus T (temperature) for the aqueous solution.

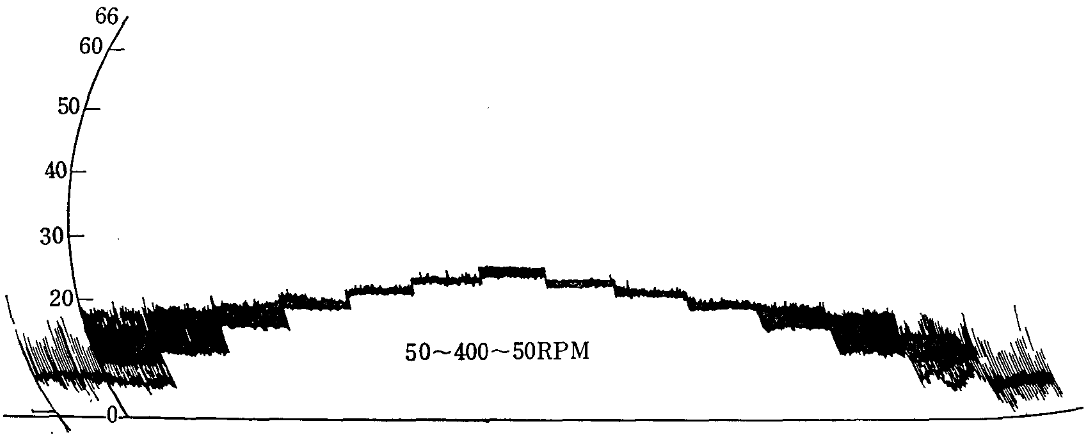

Fig. 6. The diagram obtained by the concentric cyliner viscometer $2R_1=3.9$cm, $2R_2=4.0$cm and $L=5.0$cm. The diameter of the wire is 0.6mm. The concentration of the aqueous solution is 10%, and the temperature is 50°C.
The diagram shows the Weisenberg phenomenon.

where $\Delta(F)$ is the correction term which is zero for Newtonian liquids and can be elaborated by using the following equation,

$$\Delta(F) = k_1(d\log\varphi_a/d\log F) + k_2(d\log\varphi_a/d\log F)^2, \cdots\cdots (4)$$

$$k_1 = (s^2-1)(1+2\ln s/3)/2s^2, \cdots\cdots (5)$$

and

$$k_2 = (s^2-1)\ln s/6s^2. \cdots\cdots (6)$$

Log g(F) in plotted as a function of log 4η of the aqueous solutions in Fig. 4. According to Dintenfass,[3] the type of the plots is called as "(Thixotropic) thixotropic-Newtonian". This tact seems to indicate that aggregated fluid drops of methylcellulose are suspended in a simple liquid, water. Viscosity decrease with increasing rates of shear is due to disagregation of the drops and decrease of the crowding effect.

Fig.5 shows the viscosity decrease with increasing temperature below the temperature of ca.50°C.

On the other hand, the mode of the flow of the aqueous solution seems to be changed to dilatant above the temperature of ca. 50°C. It is supported by the Weissenberg phenomenon as shown in Fig. 6. and attributed to the microgels which are formed by elevating temperature.

The statement mentioned above can be supported by the behaviors of the benzylalcohol solution. In Fig. 7, log g(F) is plotted as a function of log 4η of the 5% benzylalcohol solutions in the temperature range from 20°C to 80°C. While the viscosity of the aqueous solutions above 50°C cannot be measured because of the weissenberg

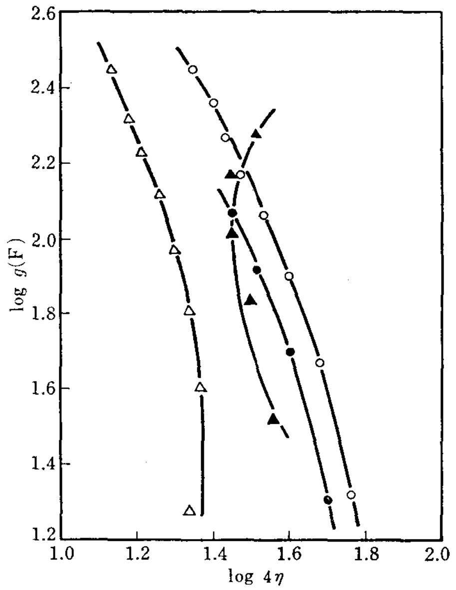

Fig. 7 The plots of log g (F) versus log η for the 5% benzyl-alcohol solutions. Open circles: 20°C, Closed circles: 40°C, Open triangles: 60°C, anp Closed triangles: 80°C.

phenomenon, that of the benzylalcohol solution can be measured up to 80°C. In the latter solution the microgels formed may be sufficietly dispersed. The log-log plot of g(F) versus 4 η at 80°C in Fig. 7 shows the "(Dilatant) thixotropic-Newtonian" type.[3] Nameny the mode of viscosity of the solution at 80°C became to include dilatancy. Also Fig.8 shows the plots of log 4 η versus temperature of the benzylalcohol solution. It is clear that the temperature dependence of the viscosity of the solution had a minimum near 60°C. This result seems to correspond to the change of the viscosity behavior at 80°C, for which a possible explation is the gelation in the solution at the high temperature.

From these results, it could be concluded that the flow of the aqueous solution methylcellulose "Metolose 90 SH 15000" below ca. 50°C was thixotropic due to the molecular aggregates and the hydrogen bonds. Above the temperature, however, the microgels seems to be formed in the solution and the mode of the flow became dilatant.

Further work is required to discuss with the present results the properties of foodstuffs, in which methylcellulose is used.

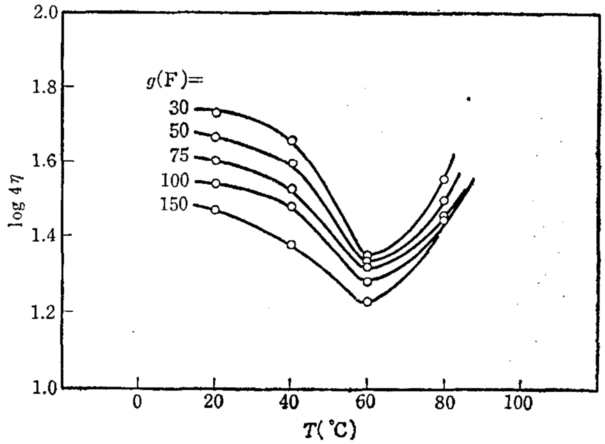

Fig. 8 The plots of log 4 η versus T (temperature) for the 5% benzylalcohol solutions.

SUMMARY

The viscosities of concentrated aqueous solutions of methylcellulose "Metolose 90 SH 15000", was measured by a concentric cylinder viscometer. This result was compared with those of benzylalcohol solutions. The mode of the flow below ca 50°C was thixotropic and that above the temperature was dilatant. The behavior seemed to be due to the aggregates and microgels formed in the solutions.

REFERENCES

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3) L. Dintenfass, *Fea. Proc.*, **25**, 1054 (1966)

抄　　録

食品の構造性改良剤・安定剤として広く用いられているメチルセルロースの濃厚水溶液の粘度測定を行なった。粘度計は Coutte 型 回転粘度計（島津ユニバーサルレオメータ，UR-I 型）を用いた。その結果，約50°C 以下の粘性挙動はチキソトロピイを示したが，その温度以上ではダイラタンシイが現れた。前者は主として溶質分子溶媒分子間の水素結合，後者は温度上昇に併うミクロゲルの生成によるものと思われる。このことは同試料のベンジルアルコール溶液の粘性挙動からも示された。